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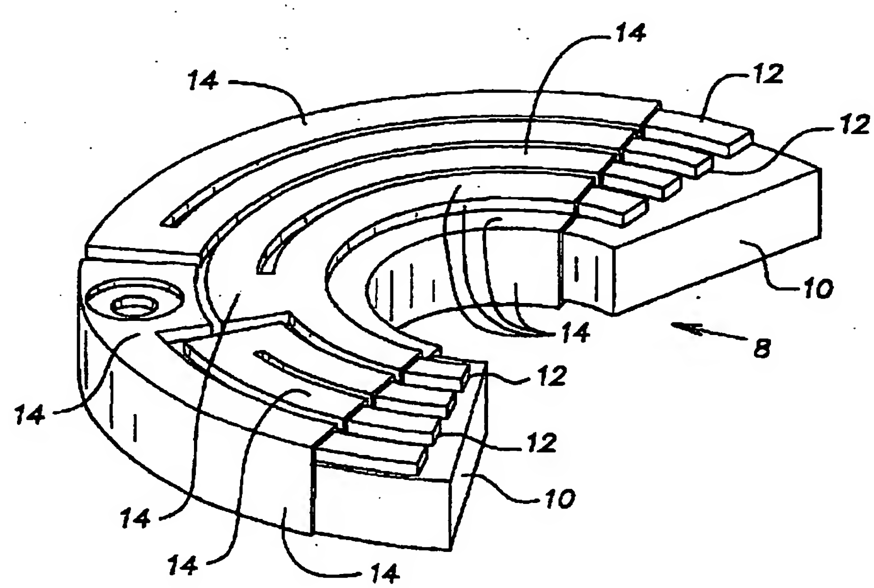
(54) Title: ARTICLES COATED WITH ALUMINUM NITRIDE BY CHEMICAL VAPOR DEPOSITION



(57) Abstract: An article with a chemical vapor deposition (CVD) aluminum nitride coating (16) is disclosed. The article is a heating element, wafer carrier, or electrostatic chuck. The article has a substrate (10) made of nitride of aluminum or boron, and further has one or more graphite elements (12) for resistance heating (12, 28) or electromagnetic chucking (30) or both. A pyrolytic boron nitride layer (14) may be provided between the substrate (10) and the CVD aluminum nitride coating (16), and may either encompass or exclude the graphite element or elements (12).

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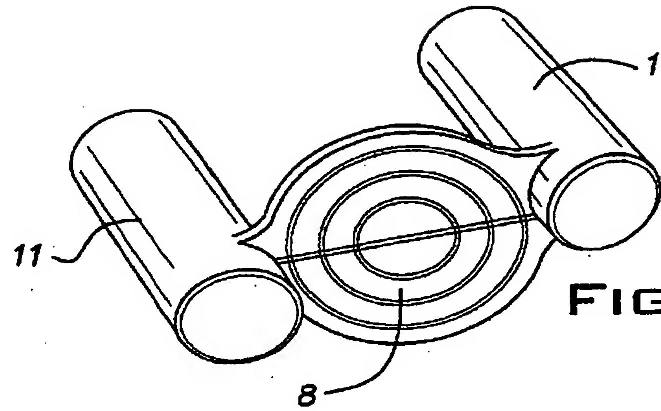

FIG. 1

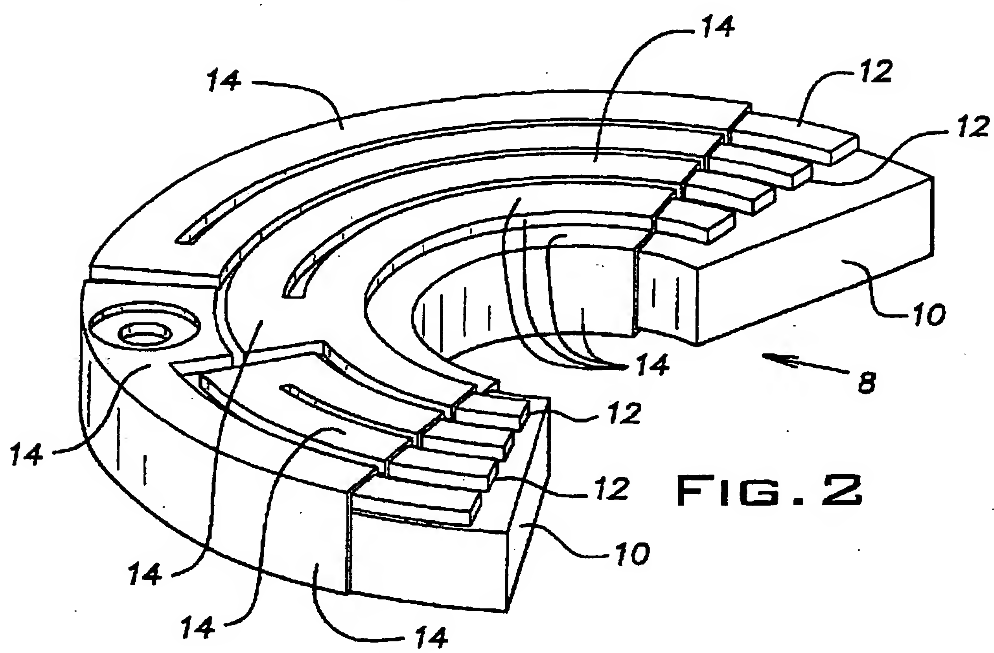

FIG. 2

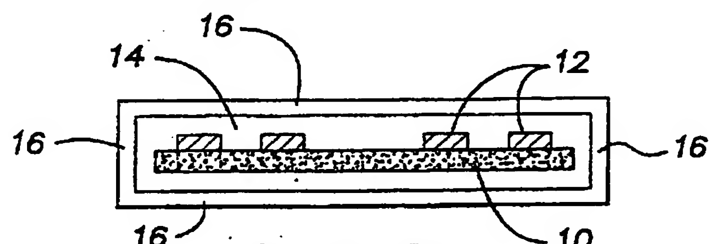

FIG. 3

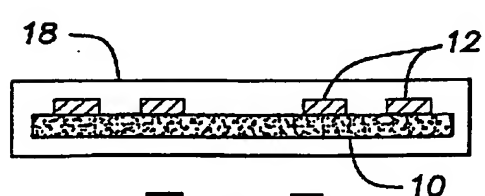

FIG. 5

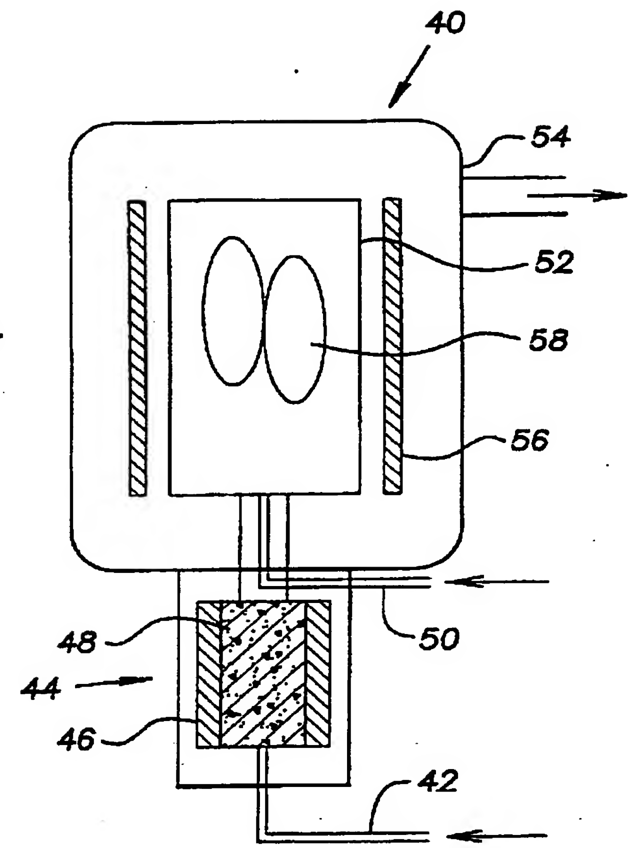

FIG. 4

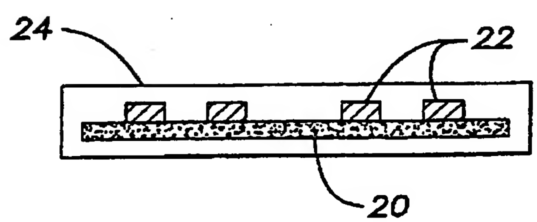

FIG. 6

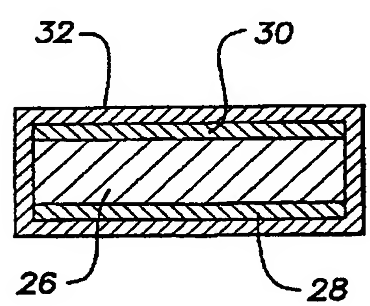

FIG. 7

ARTICLES COATED WITH ALUMINUM NITRIDE BY CHEMICAL VAPOR DEPOSITION

FIELD OF THE INVENTION

The invention relates generally to articles having an aluminum nitride coating provided by chemical vapor deposition, and more particularly to heating units, wafer carriers, and electrostatic chucks having such a coating.

BACKGROUND OF THE INVENTION

The manufacture of computer integrated circuits (computer chips) requires deposition and selective removal of many layers of material. Various components are used in the equipment that applies these thin films to silicon wafers. They include heating elements, electrostatic chucks, and wafer carriers.

During wafer coating, some of the materials that are applied to the wafer or chip also deposit on the equipment in the deposition chamber, such as the heating equipment. This requires periodic cleaning of the equipment, which is commonly done using high energy gas plasma. The most aggressive plasma uses a fluorine-bearing gas such as NF_3. This produces a fluorine plasma, which cleans the chamber but also attacks the components of the equipment. This erosion limits the life of the components and the equipment. It would be desirable to extend the service life of components and equipment by use of a suitably durable coating.

SUMMARY OF THE INVENTION

A coated article is provided. The coated article may be a heating element, electrostatic chuck, or wafer carrier. The article has a body containing a substrate and a graphite element, and also has an outer coating of aluminum nitride provided by chemical vapor deposition. The outer coating protects the article against chemical attack, for example by fluorine plasma.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a perspective view of a heating element suitable for use in the present invention.

Fig. 2 is a perspective view of a portion of the heating element in Fig. 1 on a larger scale, partially cut away to reveal components.

Figs. 3, 5, 6 and 7 are partial schematic cross-sectional views of embodiments of the invention.

Fig. 4 is a schematic view of an apparatus for performing chemical vapor deposition.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE INVENTION

In the description that follows, when a preferred range, such as 5 to 25, is given, this means preferably at least 5, and separately and independently, preferably not more than 25. As used herein and in the claims, the term "adjacent" includes both direct contact and lying near, as where an intervening layer exists between two layers or objects. An example of this latter situation is shown in Figure 3, wherein an outer layer of aluminum nitride 16 is adjacent the pyrolytic boron nitride substrate 10 and pyrolytic graphite resistors 12, and a layer of pyrolytic boron nitride 14 is disposed between the substrate 10 and the outer layer 16.

The invention concerns a coated article. The coated article may be a heating element, an electrostatic chuck, a wafer carrier, or similar article. In each case the article has a body containing a substrate and a graphite element, and also has an adjacent coating of aluminum nitride provided by chemical vapor deposition.

Fig. 1 shows a conventional heating element known in the art, such as a Boralectric brand pyrolytic boron nitride resistance (PBN) heating element available from Advanced Ceramics Corporation, Cleveland, Ohio. The heating element has a resistor 8 and a pair of connector posts 11, and is for uses such as heating silicon wafers during chemical vapor deposition of surface layers. The connector posts act to transmit electricity from a source at their base to the resistor. This PBN heating element and its construction and uses are described in more detail in U.S. Patent No.

5,343,022, the contents of which are incorporated herein by reference in their entirety.

The resistor 8 of the heating element is shown in more detail in Fig. 2, which illustrates a resistor having a PBN substrate 10 about 0.02-0.12 inches, more preferably about 0.05 inches thick and an electrically conductive serpentine pyrolytic graphite (PG) element 12 about 0.001-0.006 inches, more preferably about 0.002-0.003 inches thick, mounted on the substrate. The pyrolytic graphite element in a heater is a pyrolytic graphite resistance element or heating element with typical resistance known in the art. The PG resistance element is provided by chemical vapor deposition (CVD), and generally is machined into the desired (serpentine) configuration. The substrate and the resistance element form the body of the resistor. The body is substantially covered by a uniform protective PBN coating 14 about 0.005-0.04 inches, more preferably about 0.01-0.02 inches thick provided by CVD encapsulating the heating unit. This PBN coating 14 resists oxidation, provides electrical insulation, chemical and mechanical protection and minimizes the opportunity for carbon contamination. See also U.S. Patent Nos. 5,882,730 and 5,702,764, the contents of which are incorporated herein by reference.

One aspect of the invention is illustrated in Fig. 3, which shows the PBN heating unit of Figs. 1 and 2 coated with an outer protective coating 16 of aluminum nitride deposited by chemical vapor deposition (CVD-AlN). As shown in Fig. 3, there is a body comprising a substrate 10 and PG element 12. The body is coated with a PBN layer and the an CVD-AlN coating. All or substantially all of the exterior surface of the article is covered by the outermost CVD-AlN coating.

An article according to the invention is used in the processing of silicon wafers. As part of this processing involves layering of materials on the wafer by chemical vapor deposition, the article is also subject to being coated with the materials during the processing. It becomes periodically necessary to clean the article. The process of layering

materials on the wafer is generally not damaging to the article. However, harsh cleaning compositions such as NF_3 plasma are often used to clean the surface of these articles. This cleaning is typically undertaken after 30 to 40 process hours, or hours spent processing wafers. The article is then typically subjected to plasma cleaning for 1-2 cleaning hours or less. An article coated only with PBN is typically damaged sufficiently to require replacement after exposure to NF_3 plasma for 50 to 100 cleaning hours. The CVD-AlN coating is considerably more resistant to attack by NF_3 plasma than a PBN coating, and in testing has shown no detectable damage after 12-24 cleaning hours using NF_3 plasma. An article according to the invention preferably has sufficient CVD-AlN coating to effectively survive, that is, to maintain the article in a protected condition such that the coated article does not need to be replaced, for at least 10, 25, 50, 100, 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1500, 2000, 3000, or 4000 cleaning hours, that is, hours of NF_3 plasma attack during cleaning of the article. To achieve this, the CVD-AlN outer coating 16 is preferably about 10-100 microns, more preferably about 30-80 microns, more preferably about 50-60 microns thick.

The process of applying a CVD-AlN coating is well-known; see, for example, U.S. Patent Nos. 4,950,558; 5,672,420; 4,239,819; 5,178,911; 4,172,754; and 5,356,608, the contents of which are incorporated by reference. Fig. 4 illustrates schematically a CVD-AlN process using $AlCl_3$ and NH_3. In summary, the vapor deposition process is performed in a reactor 40 having a chlorination chamber 44 in communication with a deposition chamber 52. The deposition chamber is contained within a vacuum chamber 54, which is connected to one or more vacuum pumps. Before beginning the process, the coating substrate 58 is placed in the deposition chamber 52 and the chlorination chamber 44 is loaded with a bed of aluminum particles 48. The vacuum chamber and deposition chamber are then evacuated.

To begin the process, the chlorination chamber 44 is heated to a temperature between 200° C and 400° C by resistive heating elements 46. Chlorine (Cl_2) and nitrogen (N_2) gas are introduced through pipe 42 into the chlorination chamber. At this temperature the aluminum and chlorine form aluminum chloride gas by the reaction: $3\ Cl_2 + 2\ Al \rightarrow 2\ AlCl_3$

The aluminum chloride then passes into deposition chamber 52, which had previously been evacuated to a low pressure of about 1 to 10 torr, preferably about 2 torr. Ammonia (NH_3) and hydrogen (H_2) are also introduced into the deposition chamber through inlet 50. The temperature is maintained at 700° C to 800° C, preferably 750° C by resistive heaters 56. The coating substrate 58 is then coated with AlN as the aluminum chloride and ammonia by the reaction: $AlCl_3 + NH_3 \rightarrow AlN + 3\ HCl$

The coating builds up on the coating substrate 58 at a rate ranging from about 10 to 20 micrometers per hour. The aluminum nitride coating resulting from chemical vapor deposition is superior to that resulting from sintering or hot-pressing, as it is very dense and highly pure, and has an essentially uniform thickness. Coatings prepared as described above exhibit density from 85 to 90 percent of the theoretical crystalline density of aluminum nitride. (Theoretical AlN crystalline density = 3.26 g/cc) Preparation at a higher deposition chamber temperature of 900° C yields an even higher density, of about 97 to 100 percent of the theoretical crystalline density. Other CVD-AlN coating processes are known in the art using other techniques and materials, all of which art is incorporated herein by reference.

In another embodiment of the invention, the heating unit of Fig. 3 can be used, except that coating 16 is eliminated and PBN coating 14 is replaced by a CVD-AlN coating 18; this embodiment is illustrated in Fig. 5. The CVD-AlN coating 18 is preferably about 10-100 micrometers, more preferably about 30-80 micrometers, more preferably about 50-60 micrometers, optionally about 5-50 micrometers, thick.

Figs. 3 and 5 show the use of the conventional PBN substrate 10. Alternatively, PBN substrate 10 in Figs. 3 and 5 can be substituted by (1) a PBN-coated graphite plate (the graphite plate being about 0.10-0.75 inches thick, optionally 0.12-0.50 inches thick, the PBN coating being about 0.005-0.035 inches, more preferably about 0.015-0.020 inches thick), (2) a hot-pressed boron nitride (BN) plate about 0.10-0.75 inches, more preferably about 0.25-0.50 inches thick, or (3) a PBN-coated hot-pressed BN plate (the hot-pressed BN plate being about 0.10-0.75 inches, more preferably about 0.25-0.50 inches thick, the PBN coating being about 0.005-0.035 inches, more preferably about 0.01-0.02 inches thick).

With reference to Fig. 6, there is shown a heating element similar to those of Figs. 3 and 5, but of different materials. The heating unit of Fig. 6 has a bulk AlN substrate 20 about 0.05-0.5 inches, more preferably about 0.1-0.2 inches thick, which has been formed by hot-pressing, casting, or other known technique. The heating unit also has a pyrolytic graphite resistance element 22 about 0.001-0.006 inches, more preferably about 0.002-0.003 inches thick, provided by CVD and comparable to PG resistance element 12, and further has a CVD-AlN outer coating 24 about 10-100 micrometers, more preferably about 30-80 micrometers, more preferably about 50-60 micrometers thick. Alternatively, Fig. 6 can be an electrostatic chuck having a similar bulk AlN substrate 20 about 0.05-0.5 inches, more preferably about 0.1-0.2 inches thick, one or more CVD pyrolytic graphite electrostatic chuck electrodes 22 about 0.001-0.006 inches, more preferably about 0.002-0.003 inches thick, and a CVD-AlN outer coating 24 about 10-100 micrometers, more preferably about 30-80 micrometers, more preferably about 50-60 micrometers thick. For the design, construction, and operation of an electrostatic chuck, see U.S. Patent Nos. 5,591,269; 5,566,043; 5,663,865; 5,606,484; 5,155,652; 5,665,260; 5,909,355; and 5,693,581, the entire contents of which are incorporated herein by reference.

Optionally, the heating element of Fig. 6 and the electrostatic chuck of Fig. 6 can be combined into a single

unit. This is illustrated schematically in Fig. 7, which shows a supporting substrate 26 of the same material and thickness as bulk AlN substrate 20, heat generating layer 28 of the same material and thickness as resistance element 22 described above, electrodes 30 for an electrostatic chuck, of the same material and thickness as pyrolytic graphite conductor or electrostatic chuck electrodes 22, described above configured as an electrostatic chucking element or electrodes, and covering layer 32 the same material and thickness as CVD-AlN outer coating 24.

Optionally, the heating elements of Fig. 3, 5, or 6, the electrostatic chuck of Fig. 6, or the combined heating element and electrostatic chuck of Fig. 7 can be used as a wafer carrier to transfer wafers from place to place during the treatment process. In this case, each of the illustrated embodiments would also have an arm (not shown) and means to convey the heater or chuck or heater/chuck to the required locations. The section of the wafer carrier shown in the figures (the coated body) serves a function similar to the flat part of a spatula in conveying chips and wafers to different locations. A wafer carrier with a built-in heating element can pre-heat the wafer or maintain it at a desired temperature. A wafer carrier with a built-in electrostatic chuck allows greater rates of travel and quicker processing times. A wafer carrier combining both functions, as shown in Fig. 7, provides the advantages of both. For the wafer carrier to successfully insinuate itself into standard chip or wafer racks, however, the coated body must have a total thickness of less than about 3 mm. Thus, a wafer carrier according to the present invention must have a total combined thickness less than this total thickness of 3 mm.

Although the preferred embodiments of the invention have been shown and described, it should be understood that various modifications and rearrangements of the parts may be resorted to without departing from the scope of the invention as disclosed and claimed herein.

WHAT IS CLAIMED IS:

1. An article comprising a body, said body comprising a substrate and a pyrolytic graphite element mounted adjacent the substrate, the article further comprising an outer coating of aluminum nitride provided by chemical vapor deposition adjacent the body, the article being selected from the group consisting of a heating element, an electrostatic chuck, and a wafer carrier, the outer coating being adapted to protect the article against attack by a cleaning composition.

2. An article according to claim 1, wherein the outer coating is about 10 to 100 micrometers thick.

3. An article according to claim 1, wherein the outer coating covers substantially all of the exterior surface of the article.

4. An article according to claim 1, wherein the pyrolytic graphite element comprises an electrode.

5. An article according to claim 1, wherein the pyrolytic graphite element comprises a resistance heating element.

6. An article according to claim 5, wherein the resistance heating element is about 0.001 to 0.006 inches thick.

7. An article according to claim 1, wherein the substrate is a pyrolytic boron nitride plate.

8. An article according to claim 1, wherein the substrate is a graphite plate, and the substrate further comprises a coating of pyrolytic boron nitride.

9. An article according to claim 1, wherein the substrate is a hot-pressed boron nitride plate.

10. An article according to claim 9, wherein the substrate further comprises a coating of pyrolytic boron nitride.

11. An article according to claim 1, further comprising a pyrolytic boron nitride layer adjacent to the body and disposed between the body and the outer coating.

12. An article according to claim 11, wherein the substrate is a pyrolytic boron nitride plate.

13. An article according to claim 11, wherein the substrate is a graphite plate about, and the substrate further comprises a coating of pyrolytic boron nitride.

14. An article according to claim 11, wherein the substrate is a hot-pressed boron nitride plate.

15. An article according to claim 14, wherein the substrate further comprises a coating of pyrolytic boron nitride.

16. An article according to claim 1, wherein the substrate is an aluminum nitride plate.

17. An article according to claim 16, wherein a second pyrolytic graphite element is mounted adjacent the substrate, and the substrate is disposed between the two pyrolytic graphite elements.

18. An article according to claim 17, wherein the first pyrolytic graphite element is a resistance heating element, and the second pyrolytic graphite element is an electrode.

19. An article according to claim 1, wherein the cleaning composition is NF_3 plasma.

20. An article according to claim 1, wherein the outer coating is effective to allow the article to effectively survive at least 100 cleaning hours.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/42236

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :C23C 16/00; H02N 13/00
US CL : 118/725, 728; 414/217, 941.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 118/725, 728; 414/217, 935, 937, 941; 156/345.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,672,420 A (STINTON et al) 30 September 1997, entire document.	1-20
Y	US 5,665,260 A (KAWADA et al) 09 September 1997, entire document.	1-20
Y	US 5,663,865 A (KAWADA et al) 02 September 1997, entire document.	1-20
Y	US 5,606,484 A (KAWADA et al) 25 February 1997, entire document.	1-20
Y	US 5,591,269 A (ARAMI et al) 07 January 1997, entire document.	1-20

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search	Date of mailing of the international search report
20 MARCH 2001	16 APR 2001

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/42236

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,566,043 A (KAWADA et al) 15 October 1996, entire document.	1-20
A	US 5,343,022 A (GILBERT et al) 30 August 1994, entire document.	1-20

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/42236

B. FIELDS SEARCHED
Electronic data bases consulted (Name of data base and where practicable terms used):

USPAT, EPO, JPO, DERWENT IBM TDB:
Search terms: heating element, electrostatic chuck, wafer carrier, aluminum nitride AlN, pryolytic graphite, electrode, resistant heating element, pyrolytic boron nitrite, BN